INDUSTRIAL UTILIZATION OF MILK BY-PRODUCTS 1/

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Milk, an important agricultural commodity in most parts of the world, is produced in large quantities primarily because of its great value as a food and as a raw material for making butter, cream, cheese, ice cream, and other food products. Since milk for human consumption commands a price far in excess of the price obtainable for any other purpose, most of the milk produced is utilized directly as a food or in the manufacture of various food products. The dairy industry has found it necessary, however, to look for non-food outlets for certain milk by-products and for the occasional surplus of whole milk. The present paper discusses by-product utilization in the United States of America, and describes some of the current research aimed at improving the position of milk as an industrial raw material.

Milk Production and Milk By-products

Total milk production in the United States increased from about 109 billion pounds in 1939 to nearly 122 billion pounds in both 1944 and 1945. Total production in 1947 was 120 billion pounds. Approximately 40 percent of the total milk produced is normally separated to obtain cream for making butter. The skim milk obtained in this manner and that from which cream has been separated for direct consumption and for ice cream, make a total of about 48 billion pounds annually. In addition to this large quantity of skim milk, approximately 3 billion pounds of buttermilk--having approximately the composition of skim milk--result from the manufacture of creamery butter. The 10 billion pounds of whey produced by the cheese manufacturers contain approximately 500 million pounds of lactose, protein and salts. The total annual production of approximately 60 billion pounds of skim milk, whey and buttermilk contains more than 5 billion pounds of non-fat milk solids, that is, about 35 percent of all the milk solids produced in the United States. These by-products are relatively unattractive for human consumption because of their dilution, lack of palatibility, and perishable nature.

The great economic loss in by-products -- skim milk, buttermilk and whey -- is caused primarily by inefficient utilization rather than by actual wastage. Most of the skim milk is fed to animals on the farms and is only potentially available for manufacturing purposes. Nearly all buttermilk is fed to farm animals, either in its natural condition or in a semisolid or dried form. Considerable quantities of whey were formerly wasted, but the greater part is now fed directly to animals or dried for use as a constituent of proprietary feeds.

In attempting to expand the industrial utilization of milk products, greatest attention is naturally given to the principal dairy by-products -- skim milk and whey. This approach presents the problem of finding new and expanded profitable uses for the main constituents, casein, lactose, and whey proteins (Table I).

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for a commercial fermentation are the existence of an organism that will convert lactose efficiently into the desired product and the cost of whey in comparison with that of other carbohydrate materials such as molasses and starch hydrolyzates. Certain vitamins in whey give it an advantage in some instances.

Of the many substances obtainable from whey by fermentation, those that may be produced in yields sufficient to warrant consideration for commercial production are lactic, citric, acetic, propionic, and butyric acids, ethanol, butanol, acetyl methyl carbinol, and riboflavin (22). The only fermentation products being manufactured at present from whey in the United States are lactic acid, ethanol, vinegar, riboflavin, and butanol.

Lactic acid is produced commercially from whey with a mixed culture of a lactobacillus and a mycoderm (22). The process is efficient since the yield is more than 0.9 pound of lactic acid for each pound of lactose.

The principal uses of lactic acid are in the leather industry, where it is employed to delime hides, and in foods and beverages. The function of lactic acid in food products is to give an acid "tang" to materials such as sherbets, fruit preparations, confections, pickles, and carbonated beverages. Calcium lactate is employed in baking powder, foods and pharmaceuticals to introduce calcium for nutrition. Sodium lactate is useful in industry because of its viscosity in solution and its ability to absorb and hold atmospheric moisture. Sodium lactate solutions have been substituted for glycerol in textile printing and in papermaking. Because it corrects acidosis yet does not produce alkalosis, it is sometimes used for indigestion. It acts as a buffer in preventing undesirable reactions and decomposition of certain drugs in the alimentary tract. By a relatively new process, copper lactate can be used to electroplate any desired color. Iron lactate furnishes iron in nutrition. Various metal lactates have found use as mordants.

Lactic acid, a versatile chemical by virtue of its two functional groups, can be converted into various products of actual or potential industrial importance (6). These include solvents, plasticizers, alkyd resins, low pressure laminating resins of the allyl type, vinyl polymers and copolymers, humectants, insect repellents, and acrylic esters. The acrylic esters can be transformed by polymerization or copolymerization into polymeric plasticizers, rigid plastics, and elastomers. The acrylic elastomers, Lactoprene EV and Hycar PA, are superior to most rubbers in resistance to deterioration caused by heat, oxidation, light, ozone, mineral oils, and repeated flexing.

Ethyl alcohol can be made from whey in 84 to 90 percent of the theoretical yield, by yeasts such as Torula cremoris. The protein, spent yeast, and distillation residues are suitable for feed. In making spirit vinegar from whey alcohol, the dilute alcohol is allowed to trickle over beech shavings or birch twigs impregnated with the acetic acid organism. Passage of air through the vinegar converter accelerates the fermentation (22).

The total production of industrial alcohol in 1945 and 1946 in the United States was more than 500 and 200 million wine gallons, respectively (1, 2). The numerous industrial chemicals obtainable from ethanol have been summarized by Hatt (10).

The riboflavin content of whey can be increased by fermentation with Clostridium acetobutylicum. A yield of at least 30 micrograms of riboflavin per gram of whey can be obtained. About 30 percent of the lactose is converted during the fermentation into alcohols and acetone. Two-thirds of these compounds is butanol, which is sufficiently valuable for recovery by distillation. Butanol is in great demand as a starting point for making many industrial products, including esters of great value as solvents and plasticizers.

Besides its use in the manufacture of coated papers, casein is used, though less extensively, in the manufacture of such products as washable wall papers, box papers, water-resistant papers, and playing cards (4).

Casein in Adhesives (21):--Solutions of casein in alkalies containing enough of the protein to give a suitable viscosity can be used as glue. Such a glue compares favorably in strength with animal glue, but is not water resistant. A considerable degree of resistance to water can be imparted to casein glue, however, by modifying the simple formula, and these improved casein glues have proved to be widely useful in industry. Prepared casein glues are sold in the form of dry mixtures requiring only the addition of water before use. They are usually composed of casein, lime and a number of alkaline salts. Various chemicals have been used to improve the property of water resistance, and many different colloidal materials with adhesive properties can be mixed with casein to modify the properties of the resulting glue. It has thus been possible to adapt casein glues to a variety of specialized uses in industry.

Casein glues are used in the woodworking industry, in gluing paper and in many other fields.

Casein Paints (21):--The use of casein as a vehicle or binder for paint dates back to ancient times. Modern casein paints consist essentially of aqueous alkaline dispersions of casein as a vehicle plus suitable pigments. Marketed either in the form of a dry powder or as a soft paste, casein paint mixtures require only the addition of water before application. Newer paints of this type, that is, paints to be thinned with water, are emulsion paints in which the liquid portion is an oil-in-water emulsion and casein is the emulsifying agent to prevent separation of the liquid phases. Each of these paints--dry powder casein paint, paste casein paint and oil-containing casein paint--possesses certain advantages, and all are used extensively. In both cost and utility, casein paints stand between calcimines and flat oil paints.

Casein Fiber:--Methods for the conversion of amorphous proteins into fibers have long been known. In 1898 Millar prepared protein fibers by extruding heated protein-water mixtures into air, and in the following year he obtained two patents covering manufacture of a casein fiber by spinning a 50 percent solution of casein in glacial acetic acid into air. Shortly afterward Todenhaupt made casein fibers by extruding an alkaline solution of casein into an acid bath.

Present-day methods for spinning alkaline solutions of proteins, which are largely due to the investigations of Ferretti, Whittier and Gould, and Atwood, represent refinements of this early work. A recent paper by Peterson, et al. (18) reviews the preceding developments and evaluates some of the factors contributing to the strength of casein fiber.

Casein fiber is produced essentially as follows. An aqueous alkaline solution of casein of suitable viscosity is extruded through the small holes of a spinneret into a coagulating bath containing acid and salts. The continuous casein filaments so produced are then subjected to various treatments, which may include stretching, hardening (or tanning) with formaldehyde and aluminum salts, and acetylation. The fiber is then cut into the desired staple length. Alternatively, according to a recent report from this Laboratory (19), it is possible by an accelerated hardening process and the utilization of the centrifugal pot employed in rayon spinning, to produce a continuous-filament, silk-like, casein yarn.

Recent research at this Laboratory has been directed toward the improvement of casein plastics. Its objective has been to convert casein by chemical modification into derivatives which could be compression molded directly into finished articles with improved resistance to water. Thus, casein was treated with lower fatty acid anhydrides (9), higher fatty acid chlorides (8), potassium cyanate (11), and with formaldehyde and organic plasticizer (11). Some success has attended these efforts.

Miscellaneous Uses of Casein (4):--Casein is used in seasonings and pigment finishes in the leather industry, in finishing and sizing operations in the textile industry, as a spreader, sticker and emulsifier in insecticides, as an emulsifying agent in emulsion polymerization of synthetic rubber, as an adhesive for rayon cord in rubber tires, as a binder in printing inks, as a raw material for the production of protein hydrolyzates of high biological value, and for many other purposes.

Whey Proteins

The whey proteins, which remain in skim milk after casein has been removed, have not generally been considered as individual substances but have been designated as "lactalbumin" or heat-coagulable proteins of whey. It has been known for some time, however, that whey contains globulin as well as albumin and smaller quantities of less well defined proteins. Thus, in 1934 Palmer (16) isolated from the albumin fraction of milk whey a crystalline protein, insoluble in water but soluble in very dilute salt solution, to which the name beta-lactoglobulin was assigned (3). The yield of uniform crystalline material was as much as 0.18 percent (about 35 percent of the total coagulable protein or about 60 percent of the total albumin fraction). It is now believed that beta-lactoglobulin is the major component of the whey proteins, and that albumin (17), globulin (17) and conjugated proteins (20) are present in smaller amounts.

The proteins in whey, although present to the extent of only 0.6 percent, represent another possible source of industrial protein. At present these proteins are not separated from whey in large quantities. Limited amounts are prepared as heat-coagulated protein, which is incorporated into feeds or hydrolyzed to amino acid mixtures of excellent nutritive quality. Since some 50 million pounds of protein occur in whey, which is either used in stock feeds or wasted, many attempts toward the commercial recovery of this potentially useful protein have been made. Recent efforts in this direction may be illustrated by the investigations of McMeekin, Gordon, and Leviton. McMeekin (14) showed that organic sulfates and sulfonates of sufficiently high carbon content, such as dodecyl sulfate, were excellent precipitants for whey proteins; Gordon (7) proposed the use of hexametaphosphoric acid for the isolation of water-soluble whey protein. Neither of these methods, however, has found commercial application. In a different approach to the problem, Leviton (12) has suggested the use of dried whey or dried skim milk for the preparation of soluble whey protein. The lactose in dried whey is extracted with ethanol, leaving the residual whey proteins in water-soluble form. Dried skim milk may serve as the source of a similar product, but details of this method have not yet been published (13). More efficient utilization of whey protein awaits the discovery of some inexpensive method for separating the material in a commercially useful form.

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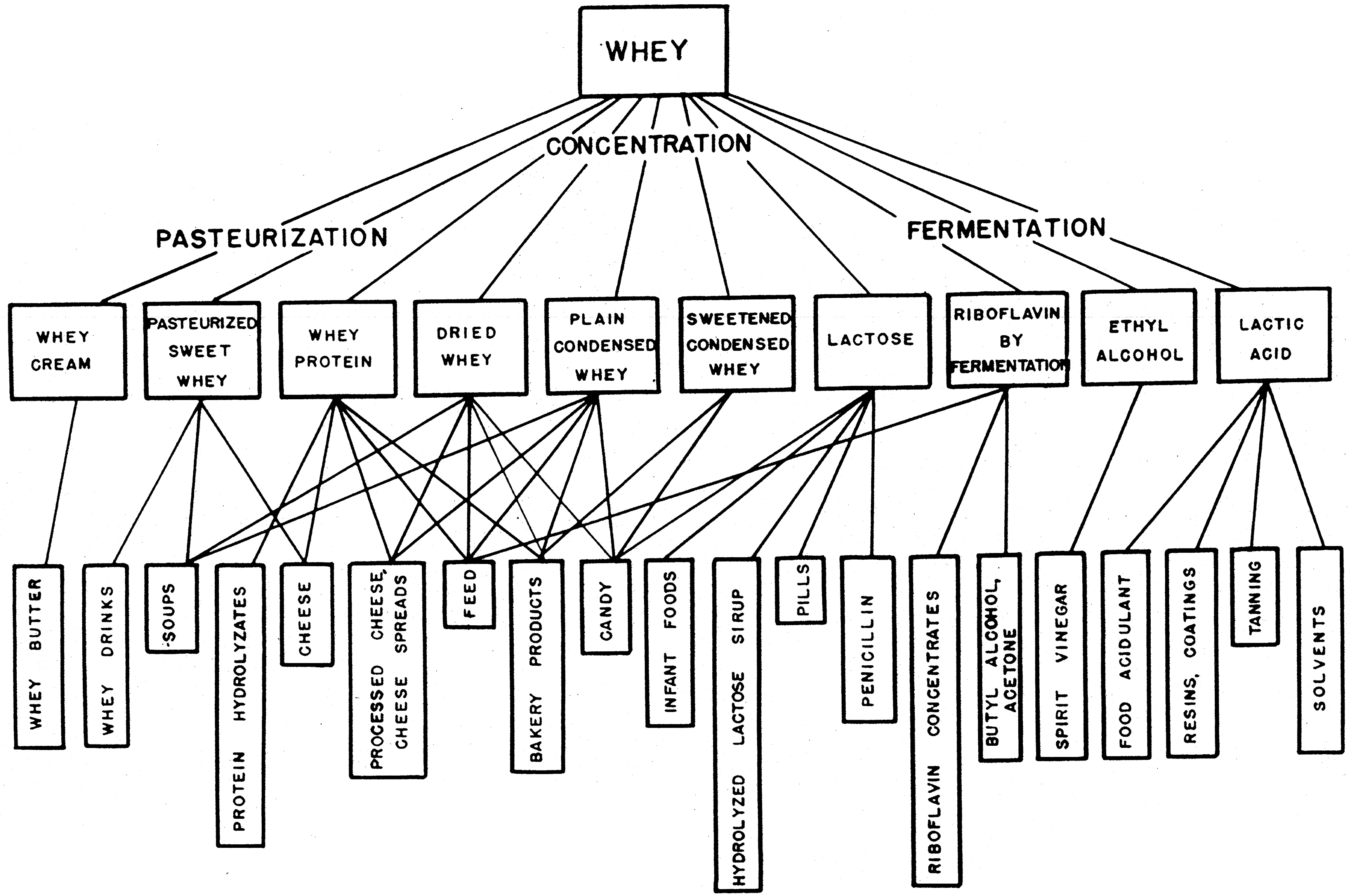

FLOW SHEET OF PRODUCTS FROM WHEY

(ADAPTED FROM WEBB and WHITTIER)